Tutorial on Upgrading of Oilsands Bitumen

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What is Oilsands Bitumen?

- Heavy crude oil extracted from oilsands
- High viscosity, high sulfur oils
- Major production from mining near Fort McMurray, Alberta
- Also produced at Cold Lake and Peace River
Why Upgrade Bitumen?

- Oil refineries are designed for lighter crudes (density < 950 kg/m$^3$)
- Bitumen has density over 1000 kg/m$^3$, over 4% sulfur, viscosity 1000x light crude oil
- Needs upgrading to sell to most refineries
Bitumen and Heavy Oil Upgrading

**Upgrading:** any fractionation or chemical treatment of bitumen or heavy oil to increase its value

- Minimum objective: reduce the viscosity to allow shipment by pipeline without adding a solvent
- Maximum objective: process to give a crude oil substitute of high quality (a “synthetic crude oil”)
Bitumen and Heavy Oil Upgrading

- **Minimum upgrading approach**
  - Reduce viscosity and control solids and water
  - None in operation; research underway on simple, small scale processes

- **Full upgrading approach**
  - Reduce sulfur and maximize distillable oil
  - Large expensive plants much like refineries

- **Focus on oil components that are too heavy to distill** (boiling point over 524 °C)
Bitumen Properties

- Up to 1/2 of the bitumen can be recovered by distillation under a vacuum
- The residue contains large molecules, with molecular weights over 400
- Complex mixture of chemical species, including aromatics, substituted aromatics, organic sulfur and nitrogen compounds
# Sulfur, Nitrogen and Metals in Residue Fraction of Feeds

<table>
<thead>
<tr>
<th></th>
<th>Sulfur, wt%</th>
<th>Nitrogen, wt%</th>
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<tbody>
<tr>
<td>Athabasca</td>
<td>5.14</td>
<td>0.56</td>
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<tr>
<td>Cold Lake</td>
<td>5.10</td>
<td>0.45</td>
</tr>
<tr>
<td>Lloydminster</td>
<td>4.69</td>
<td>0.53</td>
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<tr>
<td>Peace River</td>
<td>7.02</td>
<td>0.63</td>
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<table>
<thead>
<tr>
<th></th>
<th>Metals, ppm</th>
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<tbody>
<tr>
<td></td>
<td>Nickel</td>
<td>Vanadium</td>
</tr>
<tr>
<td>Athabasca</td>
<td>150</td>
<td>290</td>
</tr>
<tr>
<td>Cold Lake</td>
<td>200</td>
<td>490</td>
</tr>
<tr>
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<td>140</td>
<td>190</td>
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<tr>
<td>Peace River</td>
<td>130</td>
<td>410</td>
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</table>
Asphaltenes in Bitumen

- Dilution of Alberta bitumens in n-pentane or n-heptane gives 10-20% of brown/black solid precipitate
- This fraction is called “asphaltene”, contains highest molecular weight (up to 5000) and most polar components in the oil
- Asphaltenes are very reactive during processing
Asphaltenene molecules

Based on Sheremata et al., 2004; Strausz 1999
Upgrading Steps

- Large molecules that will not distill (called “Residue”) must be *cracked* to give lighter molecules
- Cracking takes place in the *primary upgrading* step at over 400 °C
- Cracking products rich in sulfur and nitrogen, so *secondary upgrading* is required to get sulfur below 0.5%
General Upgrading Scheme

Feed Separation
- Desalting
- Distillation
- Deasphalting

Primary Upgrading
(Vacuum Residue Conversion)
- Thermal cracking
- Coking
- Hydroconversion

Secondary Upgrading
- Hydrotreating
- Hydrocracking

Environmental Controls
- Sulfur removal and conversion
- Sour water

Utilities
- Hydrogen
- Steam
- Power

Waste Heat

Extraction

Sour Medium Crudes

Sweet Light Crudes

Heavy By-Product*

Sulfur By-Products

Natural Gas

* Heavy By-Product = Coke, Asphaltenes, or Vacuum Residue
Upgrading Technologies

Bitumen Upgrading

Separations
- Distillation
- Asphaltene and solids removal

Reactions
- Ultra Low T <100°C
- Low T 100 - 350°C
- Moderate T 350-470°C
- High T > 470°C
- Bioupgrading
- In situ catalysis
- Liquid Phase Low/No Coke
- Vapor+Liquid Coking

Commercial technology
Under development

Oil Sands Upgrading Chair
Suncor Base Plant and Millennium

Oil Sands Upgrading Chair
Long Lake Upgrader

Diluted Bitumen

Atmospheric and Vacuum Distillation

Gas Oil

Deasphalter

Asphalt

Deasphalted oil

Thermal Cracking

Gas Oil

Hydrotreater + Hydrocracker

H₂S

Sulfur Plant

H₂

Gasifier

Oxygen

Sulfur

Naphtha to SAGD

Sweet Crude Oil

Syngas to SAGD Steam Generators

Sulfur

Crude Oil
Asphaltene Separations

Asphaltene and Solids Removal

- In situ VAPEX
- Solvent Deasphalting (Pumpable product)
- Paraffinic Froth Treatment (Aqueous slurry product)
- Mixed Solvents for Selective Separation
- ROSE Process
- Low Temperature
- Pressurized Operation
- Supercritical Extraction (Powder product)
- SELEX-Asp

Commercial technology
Under development
Solvent Deasphalting

- Precipitate asphaltenes using paraffinic solvents (propane to hexane; $C_3$-$C_6$)
- Solvent:oil ratio is 4:1 or higher - more solvent gives cleaner separation
- Major utility cost is solvent recovery
- Separation of oil and solvent is easy above $T_c$ of solvent, minimizing energy costs
- Nexen Long Lake only oilsands example
Moderate Temperature Processes

- **Moderate T Liquid Phase**
  - **Visbreaking** <25% Conversion
  - **Catalytic Hydroconversion**
    - **Aquaconversion (Catalytic)**
    - **Supported Ni/Mo Catalysts (50-80% conversion)**
      - **H-Oil**
      - **Slurry Catalysts >70% Conversion**
        - **ENI Slurry Technology (Recycle Mo catalyst)**
  - **Solvent Cracking**
  - **Supercritical Water**

**Colors:**
- Green: Commercial technology
- Orange: Under development

*Oil Sands Upgrading Chair*
High Temperature Processes

- **High T Processing Vapor+Liquid Phase**
  - Coking
    - Delayed Coking
    - Fluid Coking
    - Eureka Process (Liquid Coke)
  - Short Contact Time
    - Ivanhoe HTL
    - Envision IyQ
  - Catalytic Cracking
    - Redox Catalysts

**Legend**
- Green: Commercial technology
- Orange: Under development

*Oil Sands Upgrading Chair*
Processes for Primary Upgrading

- Hydroprocessing
- Thermal cracking
- Residue FCC
- Deasphalting

North America + Venezuela, 1998
Thermal Conversion

- Thermal cracking underlies all current commercial reactor technology
- Rely on hydrogen gas to stabilize products
Process Characteristics - Coking

- Low pressure, reliable, safe process
- Low operating costs
- Low liquid product yields
- Coke by product is rich in sulfur, so this material is stockpiled in mines
- Main process for CNRL, Suncor and Syncrude
A Coke Primer

**coke** (kək) *noun*
A solid residue left after incomplete combustion of petroleum etc.

Probably from Northern English dialect
*colk*, core, of unknown origin
Thermal Cracking Reactions

- Breaking a C-C bonds required to get significant upgrading
- Two types of products - one stable and one unsaturated and unstable (alkenes)
- Use catalytic hydrotreating to stabilize the unsaturated products
Coking Technologies

- Delayed coking - liquid feed cracks in a large drum, and coke accumulates at the bottom with time (CNRL and Suncor)
- Fluid coking - liquid feed is sprayed into a bed of hot coke particles (Syncrude)
Hydrogen Addition Processes

- **Hydroconversion or Hydroprocessing**
  - Combine some catalytic activity with thermal cracking

- **Hydrotreating**
  - Catalytic sulfur and nitrogen removal
  - Minimal cracking

- **Hydrocracking**
  - Gasoline production using a bifunctional catalyst
Hydroconversion

- Used by Husky, Shell, and Syncrude for primary upgrading
- Feed cracks in the presence of hydrogen and a supported-metal catalyst (Mo + Ni on aluminum oxide)
- Hydrogen suppresses coke, helps remove sulfur
Hydrotreating

- Lower temperature process, with a similar catalyst (nickel + molybdenum on a support of aluminum oxide)
- High level (>90%) removal of sulfur, >70% removal of nitrogen
- Negligible cracking
Hydrocracking

- High pressure catalytic process used by refineries (Shell Scotford, Suncor Edmonton) to convert heavy distillates into feeds for gasoline
- Catalyst gives both cracking (e.g. zeolite) and hydrogenation activity
- Higher hydrogen pressure than hydroconversion or hydrotreating